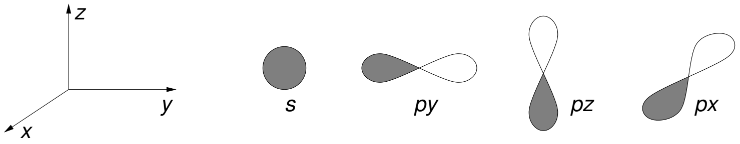
MATRL 218/CHEM 227: Class VII — Covalent Intereractions, energy bands

Ram Seshadri (seshadri@mrl.ucsb.edu)

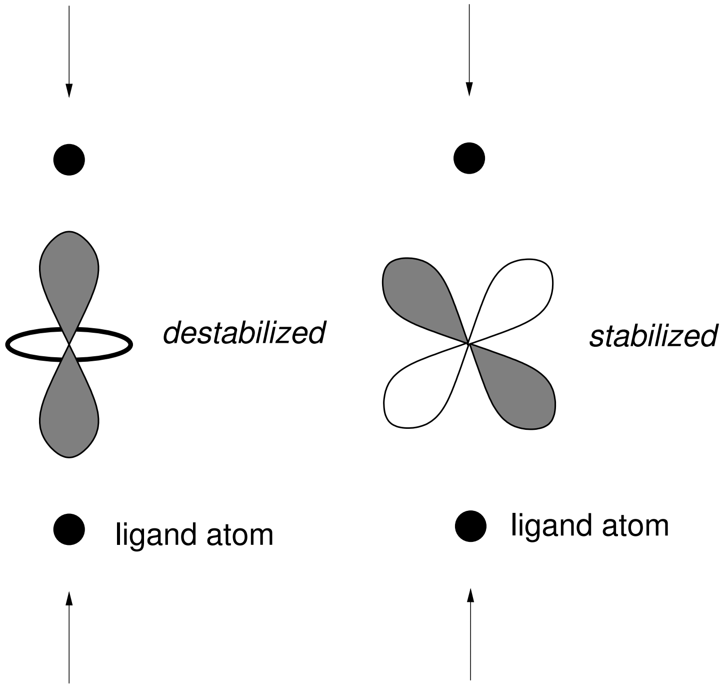
Orbitals and crystal fields

- The shapes of *s* and *p* orbitals:



- The shapes of *d* orbitals: Please see the handout.
- Crystal field theory for *d* orbital complexes:

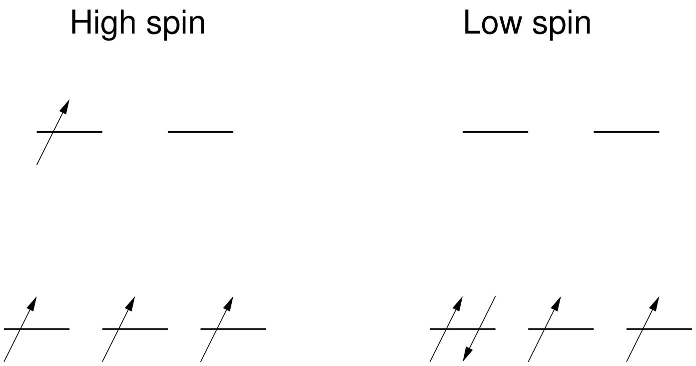
  d orbitals on free atoms are five-fold *degenerate*. This means that all *d* orbital in a free atom have the same energy. When atoms with *d* valence orbitals (transition metals) are placed in a crystalline solid, the energies of the different *d* levels are no longer *degenerate*. In the simplest theory — electrostatic *Crystal Field Theory*, the assumption is made that the ligand atoms (the anions) are point charges and when these approach a *d* orbital on the metal, that *d* orbital is destabilized.



In the above figure, ligand atoms (such as O^{2-} ions in an oxide) approach orbitals along the z axis. The d_{z^2} orbital is relatively destabilized as a result, while the d_{xz} orbital is relatively stabilized.

The precise manner in which the degeneracy of the *d* orbitals are lifted therefore depends on the local coordination of the transition metal cation — the precise geometrical arrangement of ligand atoms around the metal. See the handout for the nature of crystal field splittings corresponding to different coordinations.

- Familiarize yourself with the different ways in which these *d* levels can be filled by electrons in different transition metals.
- High spin and low spin crystal fields:

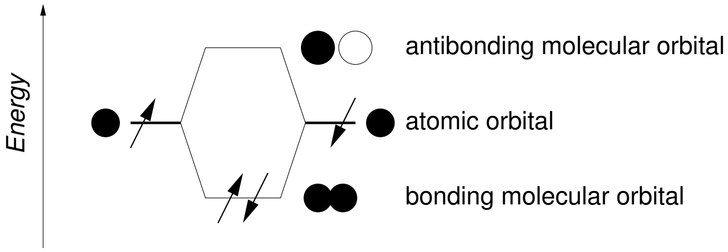


The figure shows how four *d* electrons (such as in an Mn^{3+} compound) can be distributed over the octahedral *d* orbitals. On the left, the configuration has four unpaired electrons, distributed as $t_{2g}^3\,e_g^1$. This is the high-spin configuration. On the right, the configuration is low spin with, only two unpaired electrons distributed as $t_{2g}^4\,e_g^0$

- Examples:
  - Octahedral compounds: $LaCrO_3$ ($t_{2g}^3 < e_g^0$), $LaNiO_3$ ($t_{2g}^6 < e_g^2$).
  - Tetrahedral compounds: Mn in $MnFe_2O_4$ ($e^2 < t_2^3$)
  - Square planar compounds: Pd in PdS ($d_{xz}^2 = d_{yz}^2 < d_{z^2}^2 < d_{xy}^2 < d_{x^2-y^2}^0$)

Molecules

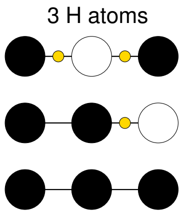
- Molecular orbitals can be formed through linear combinations of atomic orbitals:

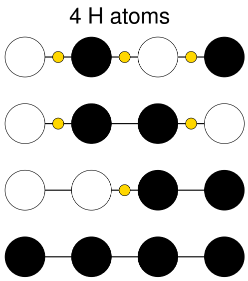


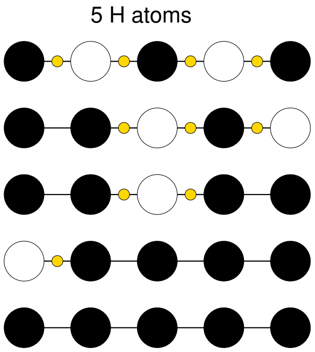
The circles are the *s* orbitals on the H atoms. We use two different colors (black and white) to represent the different possibilities of making linear combinations — addition to bond, and subtraction to antibond.

Chains

- Instead of a pair of H atoms, we can consider chains with 3, 4, 5 etc.



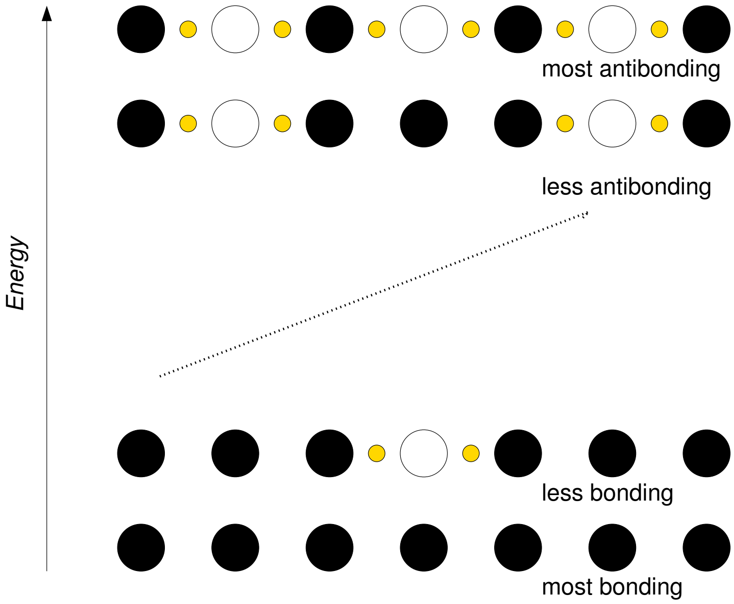




At the bottom are the most bonding molecular orbitals and at the top are the most antibonding. The little yellow circles indicate nodes. The more nodes in an orbital, the higher the energy.

1D Solids

- One can now extend this to an infinite chain:



What one then has are not molecular orbitals, but crystal orbitals. The nodes in these form a pattern. Use them to identify *wavelengths*. There are zero nodes in the most bonding orbital, so the repeat distance between nodes (which is half the wavelength) is ∞. For the most antibonding orbital, the repeat distance is a the inter-orbital/atomic distance, so the wavelength is $2a$.

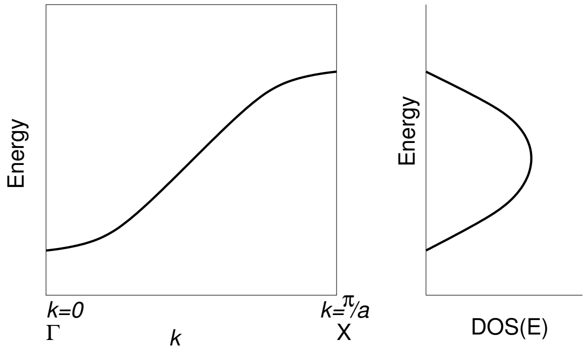
- The wavevector k appears for the first time as a solution to the free electron Schrödinger equation. k becomes quantized as a result of applying boundary conditions (see chapter 2 of Ashcroft and Mermin for a discussion).

We identify the wavelength described by the nodes as the deBroglie wavelength

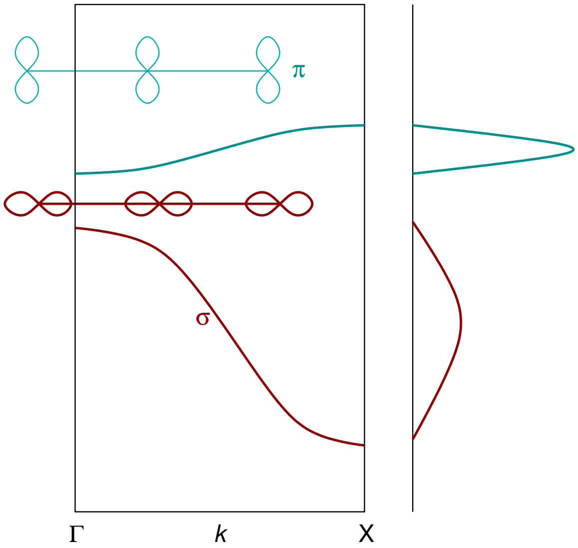
$$\lambda = \frac{2\pi}{k}$$

The most bonding crystal orbital formed from s orbitals then corresponds to $k = 2\pi/\infty = 0$ and the most antibonding, to $k = 2\pi/2a = \pi/a$. In 1 D, these points are labeled Γ and X respectively.

- *Dispersion* relations or band structures (or spaghetti diagrams) are plots of the energy as a function of the wavevector. For the 1D chain of s orbitals, we know (simply by counting nodes) that the dispersion should look like:



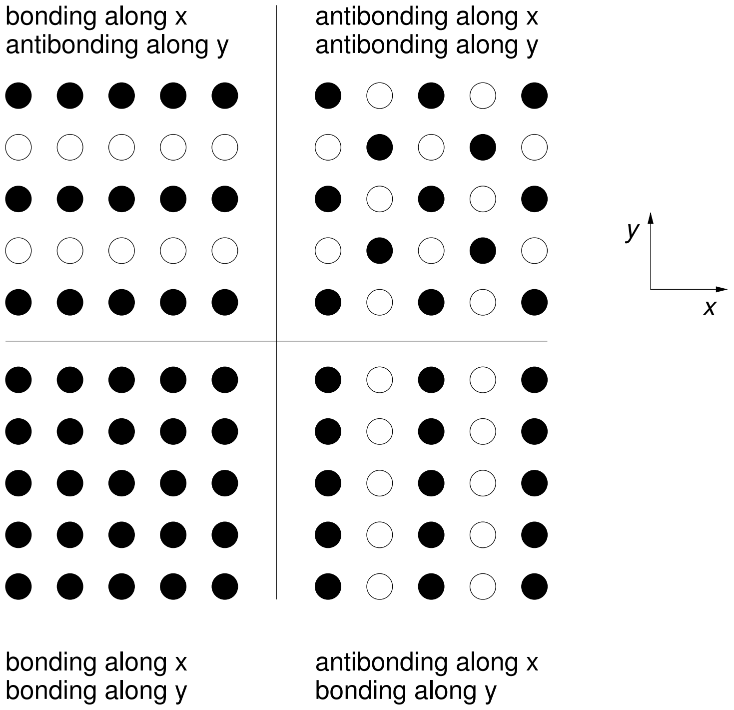
The center of gravity of a band on the energy axis is determined by the energies of the participating orbitals. The spread (dispersion) is determined by the strength of the interaction.



For example, the interaction between p orbitals can be end-on (σ) of side-on (π). σ are stronger so one obtains more disperse bands. In the scheme above, the p orbitals forming the π bonds are at a higher energy (to start with) than those that form the σ bonds.

2D Solids

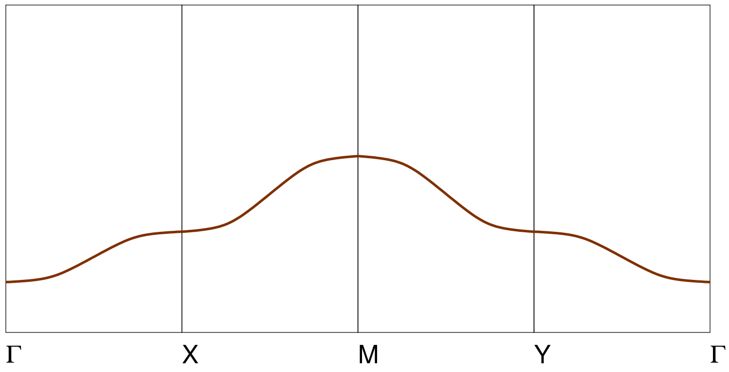
- In 2D, similar logic applies. For a square lattice of s orbitals:



Let the lattice parameter be a. Then we can consider the wavelengths in the four different cases:

  - Bonding along both x and y. The wavelengths are (∞, ∞) and $k = (0, 0)$. This is the Γ point.
  - Bonding along x and antibonding along y. The wavelengths are $(\infty, 2a)$ and $k = (0, \pi/a)$. This is the X point.
  - Antibonding along x and bonding along y. The wavelengths are $(2a, \infty)$ and $k = (\pi/a, 0)$. This is the Y point.
  - Antibonding along both x and y. The wavelengths are $(2a, 2a)$ and $k = (\pi/a, \pi/a)$. This is the M point.

The electronic band structure would look like:



For a square lattice $X = Y$, so there is no need to show the Y point. However, if the lattice is distorted (to a rectangle), the X and Y points are no longer degenerate.

Filling up the bands

Band structures/DOS involve only valence electrons. To a good approximation, core electronic levels are unaffected by the process of band formation.

Each band comprises two electrons when filled. To start filling bands with electrons, one considers the number of valence electrons in the unit cell and then starts filling from the bottommost band. The topmost filled level is the Fermi energy E_{F}.

We shall illustrate this using densities of state for a number of solids.